

UNITED STATES PATENT OFFICE.

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RED AZO DYE.

SPECIFICATION forming part of Letters Patent No. 695,811, dated March 18, 1902.

Application filed December 23, 1901. Serial No. 87,002. (No specimens.)

To all whom it may concern:

Be it known that we, PAUL JULIUS, a sub-
ject of the Emperor of Austria-Hungary, and
FRITZ GÜNTHER, a subject of the King of Prus-
sia, German Emperor, both doctors of philoso-
phy and chemists, residing at Ludwigshafen-
on-the-Rhine, in the Kingdom of Bavaria, Ger-
many, have invented new and useful Improve-
ments in Red Azo Dyes, of which the following
is a specification.

This invention relates to a new red azo dye.
This new dye may be produced by suitable
combination of diazotized 2-amido-1-naphthyl-
methane sulfo-acid (which has hitherto not
been prepared) with beta-naphthol. The salts
or lakes of this new azo dye, containing cal-
cium, barium, aluminium, lead, or the like,
are practically insoluble in water, are of a
red color having a bluish cast, and are prac-
tically unchanged in color by the action of
ordinary acids and of light, and it is this com-
bination of properties which promises to make
this new dye of value in the arts, especially
in the art of lake and pigment making.

The following is a description of the man-
ner in which this new dye may be prepared.
However, the invention is not limited to the
proportions and conditions herein given. The
parts are by weight. The temperature de-
grees are on the centigrade scale.

*A. Production of the new 2-amido-1-naph-
thyl-methane sulfo-acid.*—Rub upon one hundred
(100) parts of the sodium salt of 2-hydroxy-
1-naphthyl-methane sulfo-acid (described in
the German Patent No. 87,335) with one hun-
dred and thirty-five (135) parts of water. To
this result add ninety (90) parts of ammonia-
water containing twenty (20) per cent. of am-
monia, (NH_3). Into this introduce sulfur di-
oxid until the mixture has become slightly
acid to litmus-paper. Now add seventy (70)
parts of ammonia-water containing twenty
(20) per cent. of ammonia (NH_3) and heat up
to one hundred and fifty (150°) to one hun-
dred and sixty (160°) degrees in a closed ves-
sel for about eight (8) hours. Dilute the paste
so resulting with hot water until practically
complete solution ensues, expel the excess of
ammonia by heating, filter while hot, cool,
and add hydrochloric acid containing about

twenty-nine (29) per cent. of hydrochloric acid
(HCl) until precipitation is complete. This
precipitate may be purified, if desirable, by
boiling it with water and carbonate of soda,
filtering, and reprecipitating it from this fil-
trate by means of hydrochloric acid. In this
manner the new 2-amido-1-naphthyl-methane
sulfo-acid can be obtained. This new 2-amido-
1-naphthyl-methane sulfo-acid may be recog-
nized as follows: It is difficultly soluble in wa-
ter. Its diazo compound gives a yellow solu-
tion with sulfuric acid containing about
twenty (20) per cent. of sulfuric acid, (H_2SO_4),
which solution on boiling yields a white pre-
cipitate soluble in chloroform. Suitably com-
bined with beta-naphthol the diazo compound
yields a red coloring-matter whose sodium,
calcium, barium, lead, and aluminium salts
are quite insoluble in water.

*B. Production of the new dye from the acid
produced according to Example A.*—Dis-
solve two hundred and thirty-seven (237)
parts of 2-amido-1-naphthyl-methane sulfo-
acid (one [1] molecular proportion) in two
thousand (2,000) parts of water and fifty-five
(55) parts of calcined carbonate of soda
(about one-half [$\frac{1}{2}$] molecular proportion)
and to this add a concentrated solution of so-
dium nitrate containing sixty-nine (69) parts
of that salt, (NaNO_3) (one molecular propor-
tion.) Now introduce this mixture, stirring
the meanwhile, into two hundred and fifty
(250) parts of hydrochloric acid containing
thirty-five (35) per cent. of hydrochloric acid
(HCl) (about two and a half molecular pro-
portions) which have previously been diluted
with one hundred (100) parts of water. Af-
ter the diazotation is completed introduce
this mixture, stirring the meanwhile, into a
solution of one hundred and fifty (150) parts
of beta-naphthol (about one [1] molecular pro-
portion) in one hundred and twenty-five (125)
parts of caustic-soda lye containing thirty-
five (35) per cent. of caustic soda (NaOH) (one
molecular proportion) and add to this solu-
tion sixty (60) parts of calcined carbonate of
soda (about one-half [$\frac{1}{2}$] molecular propor-
tion) and five hundred (500) parts of water.
Stir this mixture until the formation of dye
is completed. This is usually accomplished

in the course of from three (3) to four (4) hours. It is recommended to preserve this new azo dye in the form of a paste of any suitable strength.

- 5 In the dry and powdered state this new dye is a red powder. It gives a blue-violet solution with concentrated sulfuric acid containing about ninety-six (96) per cent. of sulfuric acid, (H_2SO_4 .) This solution when diluted
10 with ice-water gives a violet precipitate, which violet precipitate becomes red on treatment with carbonate of soda. In the form of its sodium salt this new dyestuff dissolves but little in cold water, and boiling water dis-
15 solves it, but with difficulty. This new dye dyes wool from the acid-bath a red shade. The salts or lakes containing calcium, barium, aluminium, or lead are of a red color and practically insoluble in water.
20 On suitable reduction with stannous chlorid and hydrochloric acid this new dye yields 2-

amido-1-naphthyl-methane sulfo-acid, which may be recognized by the properties hereinbefore set forth.

What is claimed is—

25 As a new article of manufacture the azo dye which can be obtained from diazotized 2-amido-1-naphthyl-methane sulfo-acid and beta-naphthol, which dyes wool from the acid-bath a red shade and yields a blue-violet
30 color with concentrated sulfuric acid, and on suitable reduction yields 2-amido-1-naphthyl-methane sulfo-acid.

In testimony whereof we have hereunto set our hands in the presence of two subscribing
35 witnesses.

PAUL JULIUS.
FRITZ GÜNTHER.

Witnesses:

BERNHARD C. HESSE,
JACOB ADRIAN.